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60/439,190 9 January 2003 (09.01.2003) US
- (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).
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- (75) Inventors/Applicants (for US only): CRONIN, James, T. [US/US]; 188 Green Giant Road, Townsend, Delaware 19734 (US). ELKINS, Thomas, Shields [US/US]; 488 Gregson Place, Waverly, Tennessee 37185 (US). HELBERG, Lisa, Edith [US/US]; 111 Barnacle Court, Middletown, Delaware 19709 (US). MERKLE, James, Elliott, Jr. [US/US]; 20289 Hayes Road, Long Beach, Mississippi 39560 (US). MIRABELLA, Steven, Edward [US/US]; 613 Blue Heron Cove, New Johnsonville, Tennessee 37134 (US).
- (74) Agent: SINNOTT, Jessica, M.; E.I. Du Pont De Nemours And Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).
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(54) Title: PURIFICATION OF TITANIUM TETRACHLORIDE

(57) Abstract: The present invention is a process for reducing raw material yield losses resulting from the passivation aluminum chloride and vanadium chlorides in the chlorinator discharge in a carbochlorination process for making titanium tetrachloride.

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INTERNATIONAL SEARCH REPORT

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B. FIELDS SEARCHED

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 744 074 A (NATIONAL LEAD COMPANY) 8 June 1953 (1953-06-08) page 2, line 21-71	1, 3, 7, 10 2, 4-6, 8, 9, 11
X	<p>-----</p> <p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; JAEGER, LUBOMIR ET AL: "Purification of crude titanium tetrachloride with surface-active substances" retrieved from STN Database accession no. 56:44009 XP002281482 abstract & CS 97 317 C (JAEGER, LUBOMIR;SIMEK, BRETISLAV) 8 July 1957 (1957-07-08)</p> <p>-----</p> <p>-/--</p>	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- * & * document member of the same patent family

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Name and mailing address of the ISA

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Y	US 2 600 881 A (EDWARD RICK CHRISTIAN ET AL) 17 June 1952 (1952-06-17) cited in the application example 1 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2600881	A	17-06-1952	NONE

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"P" document published prior to the international filing date but later than the priority date claimed

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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CS 97317	C		NONE	
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US 2600881	A	17-06-1952	NONE	

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JC17 Rec'd PCT/PTO 20 JUN 2005

PURIFICATION OF TITANIUM TETRACHLORIDE
CROSS-REFERENCE TO RELATED APPLICATIONS

Cross-reference is made to U.S. Provisional Application No.
5 60/439190 filed on January 9, 2003, which is incorporated herein by
reference in its entirety.

BACKGROUND OF THE INVENTION

This invention relates to a process for the removal of multiple metal
chlorides from a crude titanium tetrachloride stream produced by
10 chlorination of titanium-bearing compounds, and more particularly to a
process wherein the removal of multiple metal chlorides occurs in a single
reaction vessel.

In the production of titanium tetrachloride, raw materials, including
ilmenite or rutile ores or other titanium-containing materials such as those
15 obtained from beneficiating these ores, are reacted with chlorine and
carbon (carbochlorination) to yield a mixture of metal chlorides in a crude
titanium tetrachloride stream, from which titanium tetrachloride of sufficient
purity may be recovered that may be used as a starting material to make
titanium metal or titanium dioxide pigment.

20 Common metal chloride impurities present in the crude titanium
tetrachloride include chlorides and complex chlorides of aluminum,
niobium, tantalum, and vanadium. These metal chloride impurities are not
susceptible to removal by distillation because of the proximity of their
boiling points to that of titanium tetrachloride or their solubility in the
25 titanium tetrachloride. They can have a detrimental impact on downstream
processes. Thus, it is important to remove them or treat them to inhibit
their detrimental properties.

Aluminum chloride, for example, is highly corrosive and attacks the
metal materials of construction in the equipment downstream of its
30 formation; thus, aluminum chloride must be rendered non-corrosive via
treatment with a passivating agent early in the processing of making crude
titanium tetrachloride.

Niobium and tantalum chlorides may condense downstream and
cause fouling problems. Conveniently these two metal chlorides may be
35 removed in the passivation of the aluminum chloride through their
preferential reaction with certain aluminum passivating agents.

Water, sodium chloride, sodium hydroxide or a mixture of these are the most common agents added to passivate aluminum chloride. The passivated aluminum compounds are more easy-to-separate from the crude titanium tetrachloride stream than aluminum chloride. Aluminum
5 passivating agents are selected to form aluminum compounds that are not corrosive to the equipment. See, for example, U.S. Patents 2,600,881; 4,125,586; and U.S. 4,521,384. Furthermore, as taught by Bonsack in U.S. Patent No. 4,070,252, use of water to treat crude titanium chloride streams also converts niobium and tantalum chlorides to species insoluble
10 in liquid titanium tetrachloride, which can be readily removed by filtration or other simple separation techniques.

Vanadium chlorides form colored species that must be removed if the titanium tetrachloride is to be used for production of titanium dioxide pigment. Typically, treatment agents are added to the crude titanium
15 tetrachloride to chemically modify these vanadium compounds so that they may be removed. Therefore, there is a body of art that teaches treatment for removing vanadium chlorides from titanium tetrachloride, but this body of art is essentially separate from that of the passivation of aluminum chloride in titanium tetrachloride.

20 The prior art in the passivation of vanadium chlorides discloses the use of catalytic metals, such as iron and copper or other agents such as activated carbons, hydrogen, hydrogen sulfide and a number of organic compounds, such as oils, esters, and amines. Examples of prior art teachings for removal of vanadium compounds from crude titanium
25 tetrachloride include the following. Swiss Patent No. 262267, published in 1949, discloses removing colored metal chlorides (Cr, and V) by treating the crude titanium tetrachloride, at an elevated temperature, with a metal-free organic compound which is carbonized by the chlorides. U.S. Patent No. 2,560,424 discloses a method to remove the colored impurities from
30 titanium tetrachloride by simultaneously adding to the crude titanium tetrachloride small amounts of aluminum metal and anhydrous aluminum chloride. Australian Patent No. 219,385 teaches the use of metallic sodium to remove vanadium impurities from titanium tetrachloride.

35 While methods have long been available for treatment of crude titanium tetrachloride, treatments to remove the metal chlorides of aluminum, niobium and tantalum have been practiced separately from treatments to remove vanadium chlorides from crude titanium

tetrachloride. The present invention is a method to remove metal chloride impurities including the chlorides of aluminum and vanadium in a way that minimizes the loss of process raw materials such as titanium containing materials, coke, chlorine, and vanadium and aluminum passivating agents.

5 The present process is more cost effective, produces less waste and more product and is the result of a simple change in the sequence of and locations for the additions of the aluminum and vanadium passivating agents.

SUMMARY OF THE INVENTION

10 The present invention provides a method in the purification of a crude titanium tetrachloride chlorinator discharge from the carbochlorination of titanium containing materials to minimize the loss of raw materials resulting from passivation of aluminum chloride and vanadium oxychloride, comprising:

15 (a) mixing into a crude titanium tetrachloride chlorinator discharge comprising vanadium chlorides and aluminum chloride:

(1) a vanadium passivating agent to passivate the vanadium chlorides present and form in the discharge one or more easy-to-separate vanadium-containing compounds,
20 and

(2) an aluminum passivating agent to passivate the aluminum chloride present and form in the discharge one or more easy-to-separate aluminum-containing compounds wherein the aluminum passivating agent is selected from the group consisting of water, water containing solutions, water
25 containing mixtures, and carboxylic acids,

with the proviso that:

(i) when, after mixing the vanadium passivating agent into the chlorinator discharge, titanium oxychloride is formed in the discharge, no aluminum passivating agent is mixed into the discharge; and
30

(ii) when, after mixing the vanadium passivating agent into the chlorinator discharge, no titanium oxychloride is formed, mixing into the discharge an amount of aluminum passivating agent to passivate the aluminum chloride and react with
35

the titanium tetrachloride to form titanium oxychloride; and

- (b) separating from the titanium tetrachloride chlorinator discharge the easy-to-separate vanadium- and aluminum-containing compounds to form a purified titanium tetrachloride.

In the present process the separation typically depends upon the phases present in the discharge and suitable separation techniques are well known in the art. Typically a distillation process is employed for vapor-liquid-solid separation, preferably selected from the group consisting of flash distillation and multi-stage distillation. The solid-liquid separation process can be a filtration or centrifugation.

The addition of the vanadium and aluminum passivating agents may be made such that the vanadium passivating agent and the aluminum passivating agent are mixed into the discharge essentially simultaneously or the vanadium passivating agent may be mixed into the discharge before the aluminum passivating agent is mixed into the discharge, or the vanadium passivating agent may be mixed into the discharge after the aluminum passivating agent is mixed into the discharge or the vanadium passivating agent may be mixed into the discharge both before and after the aluminum passivating agent is mixed into the discharge.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a method in the purification of a crude titanium tetrachloride chlorinator discharge from the carbochlorination of titanium containing materials to minimize the loss of raw materials resulting from passivation of aluminum chloride and vanadium chlorides.

The term vanadium chlorides as used herein includes vanadium oxychloride compounds and other vanadium chloride compounds that are not susceptible to removal from crude titanium tetrachloride by distillation.

In the present invention, the passivation of vanadium chlorides may be accomplished in a two step addition of the vanadium passivating agent or in a single step addition. In the two step addition, a vanadium passivating agent is mixed into the discharge in an amount sufficient to reduce, but not eliminate the vanadium chlorides present and form one or more easy-to-separate vanadium-containing compounds. When titanium oxychloride is present in the discharge treated with the vanadium passivating agent, no aluminum passivating agent is added. When titanium oxychloride is not present, an amount of aluminum passivating

agent sufficient to form titanium oxychloride is added to form easy-to-separate aluminum-containing compounds. The easy-to-separate vanadium- and aluminum-containing compounds may be separated from the discharge. Then, a second addition step of a vanadium passivating agent in an amount sufficient to passivate the remaining vanadium chlorides is made to form easy-to-separate vanadium-containing compounds, followed by a separation step to form a purified titanium tetrachloride.

In the single step addition of the vanadium passivating agent, sufficient vanadium passivating agent is mixed into the discharge to passivate all of the vanadium chlorides in a single step, and, if necessary, addition of aluminum passivating agent is made if there remains active aluminum chloride in the discharge as determined by the absence of titanium oxychloride in the discharge. In any event, all of the aluminum chloride present in the discharge must be passivated, no matter which method (two step or single step) is used to passivate the vanadium chlorides, since the presence of active aluminum chloride after this point in the overall purification process will result in corrosion of downstream equipment.

The terms passivating and passivation as used herein mean converting the vanadium- and aluminum-containing compounds present in the crude titanium tetrachloride discharge to compounds that are easy-to-separate from the titanium tetrachloride and neutralizing the compounds' adverse effects. "Easy-to-separate" typically means a solid, but it also includes compounds that may be separated from the titanium tetrachloride by distillation or removal as an adsorbed species, and the like. Surprisingly, it has been found that the product of the passivation of vanadium oxychloride in crude titanium tetrachloride discharge with an organic oil is a passivating agent for aluminum chloride. The result of this discovery according to the present invention is an improved chlorination process wherein there is the potential to save production costs by reducing the titanium yield loss while at the same time improving raw material utilization to reduce process cost and the amount waste - solid, liquid, and vapor.

In the present invention, the point of addition of the passivating agents into the flow of the chlorinator product stream, that is, crude titanium tetrachloride discharge, may be optimized for (1) the reduction

and elimination of corrosion from active aluminum chloride, (2) minimal yield losses of raw materials, and (3) to take advantage of the ability of passivated vanadium compounds to provide at least part of the total amount of passivating agent needed to control passivation of aluminum chloride, as measured by titanium oxychloride concentration.

Addition of the aluminum passivating agent is dependent on whether there is titanium oxychloride in the crude titanium tetrachloride chlorinator discharge stream. Aluminum chloride is completely passivated once titanium oxychloride is formed in the discharge. Aluminum passivating agent may be mixed into the chlorinator discharge simultaneously with the vanadium passivating agent or before addition of the vanadium passivating agent or after addition of the vanadium passivating agent. After mixing the vanadium or aluminum passivating agent into the chlorinator discharge, the discharge is analyzed for titanium oxychloride. If titanium oxychloride is formed, addition of aluminum passivating agent is not required. If no titanium oxychloride is formed, then an amount of aluminum passivating agent sufficient to passivate the aluminum chloride and react with the titanium tetrachloride to form titanium oxychloride is mixed into the chlorinator discharge.

Water is most preferred as the aluminum passivating agent in the present process. Water solutions or mixtures may be used as passivating agents even if the materials other than the water show no reactivity towards aluminum chloride.

Since some fraction of the aluminum chloride is passivated by the reaction product of vanadium oxychloride with the vanadium passivating agent, it is preferable to add only 1 to 1.5 times the amount of passivating agent to stoichiometrically react with the remaining aluminum in the discharge. More preferably the amount of aluminum passivating agent added is 1.1 to 1.3 times the stoichiometric requirement.

Organic oils have been found to be useful as vanadium passivating agents including petroleum oils, such as mineral oils and waxes, animal fat, and vegetable oils and combinations thereof. The organic oil may be hydrogenated. A specific example of a useful organic oil is hydrogenated naphthenic oil. The essential element in selecting a substance as a vanadium passivating agent is the ability of the reaction product of the passivating agent with vanadium oxychloride to function as an aluminum passivating agent. Those skilled in the art may find other organic

compounds that are functionally equivalent to an organic oil that are also useful as the vanadium passivating agent. Similarly, some inorganic vanadium passivating agents may also be useful as functional equivalents to the organic oil, so long as there are no detrimental effects, such as color
5 formation in the titanium tetrachloride, or where the passivated compounds may become re-chlorinated. Especially preferred as the organic oil vanadium passivating agent is a hydrogenated naphthenic oil.

The amount of vanadium passivating agent is based on the agent's stoichiometric reaction ratio with the vanadium chlorides. Ideally, this ratio
10 should be determined experimentally, rather than theoretically. Preferably the amount of vanadium passivating agent added is 0.8 to 1.2 times the stoichiometric quantity required to react with the vanadium chlorides to be removed from the stream being treated, which may be all or any fraction of the vanadium present in that stream. More preferably the amount of
15 vanadium passivating agent is from 0.95 to 1.1 times the stoichiometric requirement.

Regardless of the amount of vanadium passivating agent added, it is possible to calculate the amount of vanadium removal reaction products capable of passivating aluminum chloride and then reduce the amount of
20 aluminum passivating agent or reduce the addition rate by an equivalent amount which can substantially reduce titanium losses due to excess addition of aluminum passivating agents which react with titanium tetrachloride. For example, one method to calculate the amount of vanadium removal reaction products capable of passivating aluminum
25 chloride is by infrared spectroscopy, based on concentration of vanadium oxychloride in the chlorinator discharge.

Following addition of the passivating agents, there is provided a separation step wherein the easy-to-separate vanadium- and aluminum-containing compounds are separated from the titanium tetrachloride
30 chlorinator discharge to form a purified titanium tetrachloride using a vapor-liquid-solid separation process or a solid-liquid separation process. A vapor-liquid-solid separation process is typically a distillation process, preferably selected from the group consisting of flashing distillation and multi-stage distillation. A solid-liquid separation process is typically
35 filtration or centrifugation.

The separation process may occur in one or more steps. For example, depending on the order of addition of the vanadium and

aluminum passivating agents, intermediate separation steps may be performed. Particularly, in a two step addition of the vanadium passivating agent, a separation step may be performed after all of the aluminum chloride has been converted to easy-to-separate aluminum-containing compounds. A separation step is performed after the second addition of the vanadium passivating agent.

Alternatively, following a separation step after addition of vanadium passivating agent, a purge containing products from the passivation of vanadium chlorides may be used as the aluminum passivating agent.

Process control methods for the addition of the aluminum passivating agent, the vanadium passivating agent, or both can be applied to the present invention. For example, the control methods disclosed in U.S. Patent 6,562,312 are particularly useful for controlling addition of aluminum passivating agent. Therein is provided, an in-process, real time control loop capable of controlling the passivation of aluminum chloride in crude titanium tetrachloride chlorinator discharge wherein an aluminum passivating agent is mixed into the discharge in an amount sufficient to form titanium oxychloride. The amount of aluminum passivating agent added is controlled based on comparison of the titanium oxychloride concentration measured in-process with an aim point. Preferably, the concentration of titanium oxychloride is measured by an optical method selected from the group consisting of transmission filter Infrared spectroscopy, transmission Fourier Transform Infrared spectroscopy, Raman spectroscopy, Attenuated Total Reflectance Infrared spectroscopy, and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy.

The presence and concentration of titanium oxychloride may be measured by use of transmission filter Infrared spectroscopy, transmission Fourier Transform Infrared spectroscopy, Raman spectroscopy, and Attenuated Total Reflectance Infrared spectroscopy, and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy in a frequency range of from 800 to 2000 cm^{-1} .

For accuracy and precision, it is most preferred to measure the presence and the concentration of titanium oxychloride by diamond based Attenuated Total Reflectance Fourier Transform Infrared at a frequency of about 820 cm^{-1} . Diamond based attenuated reflectance means that the infrared probe or detector placed in the process stream has a diamond

element. Suitable probe units include those manufactured by ASI Applied Systems of Millersville, MD, Axiom Analytic, Inc. of Irvine, CA and others.

In the following examples VOCl_3 passivation is measured by Fourier Transform Infrared Spectroscopy (FTIR).

5 Example 1

A round bottomed flask was filled with 100 mL TiCl_4 , 0.92 g VOCl_3 (5.31 mmol), and 0.174 g AlCl_3 (1.30 mmol). The AlCl_3 was handled air-free to avoid moisture contamination. The reaction mixture was heated to 100°C. Hydrogenated naphthenic oil (ERGON Incorporated's product
10 brand Ergon H-750) was added (1.0333 g). The reaction mixture was held at temperature for 30 minutes. At this point, all of the VOCl_3 was passivated, as measured by FTIR. To determine how much unreacted AlCl_3 remained, 30 microliter (1.61 mmol) of water were added by syringe. Any AlCl_3 in solution would react with the water before TiOCl_2 was formed.
15 A total of 1531 ppm TiOCl_2 was generated from the water addition, as observed by FTIR. If all of the AlCl_3 was present, only 280 ppm should have been observed. Since an extra 1301 ppm TiOCl_2 (1.67 mmol) formed, all of the AlCl_3 had already been passivated in the solution.

Example 2

20 A round bottomed flask was filled with 100 mL TiCl_4 , 0.92 g VOCl_3 (5.31 mmol), and 1.74 g AlCl_3 (13.0 mmol). The AlCl_3 was handled air-free to avoid moisture contamination. The reaction mixture was heated to 100°C. The oil from Example 1 was added (1.0401 g). The reaction mixture was held at temperature for 30 minutes. At this point, all of the
25 VOCl_3 was passivated, as measured by FTIR. To determine how much unreacted AlCl_3 remained, 290 microliter (16.1 mmol) of water were added by syringe. A total of 6808 ppm TiOCl_2 was generated from the water addition. If all of the AlCl_3 was still present, only 2371 ppm TiOCl_2 should have been observed. Since an extra 4437 ppm TiOCl_2 (5.70 mmol)
30 formed, part of the AlCl_3 was passivated in the solution. The amount of AlCl_3 reacted was stoichiometrically equivalent to the amount of oxygen initially present in solution as part of the VOCl_3 , within experimental error.

Example 3

Water was added as an aluminum passivating agent to a crude
35 TiCl_4 stream containing metal chloride contaminants AlCl_3 and VOCl_3 produced by the chlorination of titanium-bearing ore, following discharge from the chlorinator and separation of condensable solids. Water addition

was in control by the control method described in U.S. Patent No. 6,562,312. The hydrogenated, naphthenic oil, from Example 1 (vanadium passivating agent) was added to the TiCl_4 stream at the same location as the water addition. In contrast to operating the process in the
5 absence of the vanadium passivating agent, the demand for aluminum passivating agent was reduced by 50% while reducing VOCl_3 by 20% of its original concentration.

CLAIMS

What is claimed is:

1. A method in the purification of a crude titanium tetrachloride chlorinator discharge from the carbochlorination of titanium containing materials to minimize the loss of raw materials resulting from passivation of aluminum chloride and vanadium oxychloride, comprising:
 - (a) mixing into the crude titanium tetrachloride chlorinator discharge comprising vanadium chlorides and aluminum chloride:
 - (1) a vanadium passivating agent to passivate the vanadium chlorides present and form in the discharge one or more easy-to-separate vanadium-containing compounds, and
 - (2) an aluminum passivating agent to passivate the aluminum chloride present and form one or more easy-to-separate aluminum-containing compounds wherein the aluminum passivating agent is selected from the group consisting of water, water containing solutions, water containing mixtures, and carboxylic acids,with the proviso that:
 - (i) when, after mixing the vanadium passivating agent into the chlorinator discharge, titanium oxychloride is formed in the discharge, no aluminum passivating agent is mixed into the discharge; and
 - (ii) when after mixing the vanadium passivating agent into the chlorinator discharge, no titanium oxychloride is formed in the discharge, mixing into the discharge an amount of aluminum passivating agent to passivate the aluminum chlorides and react with the titanium tetrachloride to form titanium oxychloride;
 - and
 - (b) separating from titanium tetrachloride chlorinator discharge the easy-to-separate vanadium- and aluminum-

containing compounds to form a purified titanium tetrachloride.

2. The process of Claim 1 wherein the separation process is selected from the group consisting of flashing distillation, multi-stage
5 distillation, a solid-liquid separation process, filtration, and centrifugation.

3. The process of Claim 1 wherein the vanadium passivating agent and the aluminum passivating agent are mixed into the discharge essentially simultaneously.

4. The process of Claim 1 wherein the vanadium passivating
10 agent is mixed into the discharge before the aluminum passivating agent is mixed into the discharge stream.

5. The process of Claim 1 wherein the vanadium passivating agent is mixed into the discharge after the aluminum passivating agent is mixed into the discharge stream.

15 6. The process of Claim 1 wherein the vanadium passivating agent is mixed into the discharge in an amount sufficient to reduce the concentration of, but not eliminate the vanadium chlorides present.

7. The process of Claim 1 wherein the aluminum passivating agent is comprised of a purge containing products from the passivation of
20 vanadium chlorides taken from a process step following the separation step.

8. The process of Claim 1 wherein the addition of the vanadium passivating agent and the aluminum passivating agent are controlled by a process control method.

25 9. The process of Claim 1 wherein the vanadium passivating agent is an organic oil.

10. The process of Claim 1 wherein the vanadium passivating agent is a petroleum oil, an animal fat, a vegetable oil or a combination thereof

30 11. The process of Claim 1 wherein the vanadium passivating agent is a hydrogenated naphthenic oil.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US2004/000765

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01G23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 744 074 A (NATIONAL LEAD COMPANY) 8 June 1953 (1953-06-08) page 2, line 21-71 ---	1, 3, 7, 10 2, 4-6, 8, 9, 11
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; JAEGER, LUBOMIR ET AL: "Purification of crude titanium tetrachloride with surface-active substances" retrieved from STN Database accession no. 56:44009 XP002281482 abstract & CS 97 317 C (JAEGER, LUBOMIR;SIMEK, BRETISLAV) 8 July 1957 (1957-07-08) --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *8* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Int Application No
PCT/US2004/000765

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 592 021 A (WALTER FREY ET AL) 8 April 1952 (1952-04-08) column 5, line 51-75; example 1	1-11
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/000765

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